

AD No. 20923  
ASTIA FILE COPY

UNIVERSITY OF MARYLAND  
COLLEGE PARK, MARYLAND

HIGH PRESSURE LABORATORY

TECHNICAL REPORT NO. 1

October 15, 1953

CONTRACT NO. Nonr-595(02)

The new High Pressure Laboratory of the University of Maryland, which is now being established on the campus at College Park, presents Technical Report No. 1. Since the new laboratory building is still in the process of construction, no experimental work has been possible so far.

This report therefore consists of a manuscript containing the analysis of p-v-T data and the evaluation of thermodynamic quantities of ethane, carried out by the computing staff at the University of Maryland; the experimental results were obtained from the van der Waals Laboratory of the University of Amsterdam. The manuscript will be published shortly in the Dutch journal "Physica".

ISOTHERMS AND THERMODYNAMIC FUNCTIONS OF ETHANE  
AT TEMPERATURES BETWEEN 0°C AND 15°C AND PRESSURES UP TO 200 ATM.

by A. Michels, W. van Straaten and J. Dawson

Contribution from the University of Maryland, College Park, U.S.A. and  
the van der Waals Laboratorium, Gemeente Universiteit, Amsterdam,  
Netherlands

(From experimental work carried out at the van der Waals Laboratorium,  
evaluation of the data and calculations of the thermodynamic functions  
were accomplished at the University of Maryland under Contract Nonr-595(C2).

1. Introduction. With the method described in previous papers<sup>1)</sup>, PVT data of ethane have been determined between 0° and 150° C and for pressures up to 200 atmospheres (densities up to 180 Amagat units). Ethane was prepared by electrolysis of a saturated potassium acetate solution. To remove by-products, the gas was led through concentrated alkali solution and bromine water and over solid KOH. The gas was then solidified at liquid air temperature so that non-condensable gases could be removed for the greater part by pumping. Efficient removal of the last traces of permanent gases was achieved by adsorbing the gas on activated charcoal at liquid air temperatures and desorbing again at about -60° C; here only the middle fraction was retained. The results are given for the compressibility isotherms and thermodynamic functions over the temperature and density ranges mentioned above; pressures are expressed in international atmospheres and densities in Amagat units.

2. Results. For every isotherm a power series of the form  $PV = A + Bd + Cd^2 + Zd^3 + Dd^4$  was fitted to the experimental points over the density region as far as it was measured. The coefficients of these series are given in table I. From the equations, together with the experimental PVT values and the deviation curves, table II was prepared, giving PV values at integral densities. A separate equation  $PV = A + Bd + Cd^2$  was calculated from the series (a) and (b) (densities below 50 Amagat units); the coefficients of these equations are given in table III.

With the method of computing as described previously<sup>2)</sup>, thermodynamic properties were calculated from the compressibility isotherms, using the spectroscopic data for the specific heat at zero density of Lincoln Smith<sup>3)</sup>. The results for entropy, energy, enthalpy, free energy, free enthalpy, internal kinetic energy and specific heat are given in tables IV to XI.  $S$  and  $S_1$  are estimated to be accurate to 0.04 joule mole·degree, while  $U$ ,  $U_1$ ,  $\bar{H}$ ,  $F$ ,  $G$  and  $\Delta K$  have an estimated accuracy of 10 joules mole. The error estimate for  $C_v$  and  $C_p$  is 2 joules mole·degree.

#### REFERENCES

- 1) Michels, A., Wouters, H. and de Boer, J., *Physica* 1 (1934) 587  
Michels, A., Michels, C., and Wouters, H., *Proc. Roy. Soc. A* 153 (1935) 214  
Michels, A. and Wouters, H., *Physica* 8 (1941) 923
- 2) Michels, A., Geldermans, M. and de Groot, S. R., *Physica* 12 (1946) 105  
Michels, A. and de Groot, S. R., *Appl. Sci. Res. A1* (1948) 94
- 3) Smith, L. G., *J. Chem. Phys.* 17 (1949) 139

Table I

$PV = A + Bd + Cd^2 + Zd^3 + Dd^4$   
 $d = 19-182 \text{ Am. (for } 25^\circ\text{C, } d = 19-65 \text{ Am.)}$   
 Series evaluation; with  $A = RT$

Coeff. Temp. $^\circ\text{C.}$	<u>A</u>	<u><math>B \cdot 10^3</math></u>	<u><math>C \cdot 10^6</math></u>	<u><math>Z \cdot 10^9</math></u>	<u><math>D \cdot 10^{12}</math></u>
25	1.102146	-9.17104	22.0502	26.553	-77.970
50	1.196029	-8.49790	24.5889	-0.74624	-59.028
75	1.288949	-7.83655	25.7355	-30.8991	+53.362
100	1.381125	-7.18536	25.2000	-40.3027	108.343
125	1.473581	-6.59282	24.6808	-44.6828	145.890
150	1.565715	-5.99199	23.1444	-37.2149	148.240

Table II

<u><math>T/d</math></u>	<u><math>0^\circ</math></u>	<u><math>25^\circ</math></u>	<u><math>50^\circ</math></u>	<u><math>-75^\circ</math></u>	<u><math>100^\circ</math></u>	<u><math>125^\circ</math></u>	<u><math>150^\circ</math></u>
		<u>PV</u>	<u><math>\text{C}_2\text{H}_6</math></u>				
0	1.01006	1.10250	1.19495	1.28740	1.37984	1.47229	1.56473
1	1.00000	1.09331	1.18655	1.27971	1.37280	1.46583	1.55885
2	.98999	1.08416	1.17819	1.27207	1.36580	1.45943	1.55301
3	.98001	1.07506	1.16988	1.26447	1.35884	1.45306	1.54721
5	.96020	1.05700	1.15540	1.24942	1.34505	1.44045	1.53574
10	.91143	1.01270	1.11302	1.21255	1.31135	1.40966	1.50775
15	.86375	.96961	1.07381	1.17681	1.27872	1.37992	1.48078
20	.81716	.92775	1.03579	1.14214	1.24709	1.35119	1.45475
40		.77208	.89536	1.01490	1.13179	1.24693	1.36111
60		.63599	.77356	.90524	1.03326	1.15895	1.28326
80			.67060	.81292	.95127	1.08708	1.22138
100				.58555	.73721	.88522	1.03113
120				.51718	.67712	.83483	.99112
140				.46341	.63183	.80005	.96774
160				.42385	.60201	.78230	.96292
180				.39676	.58804	.78294	.97909

Table III

$$PV = A + Bd + Cd^2$$

$d = 0.52$  Am. Series evaluation; with  $A = RT$

<u>Coeff.</u> <u>Temp.</u> <u>°C.</u>	<u>A</u>	<u>B·10<sup>3</sup></u>	<u>C·10<sup>6</sup></u>
0.000	1.010058	-10.0800	21.7571
24.988	1.102459	- 9.2208	24.0377
49.598	1.193463	- 8.4392	23.4386
74.502	1.285553	- 7.7214	22.5878
99.372	1.377518	- 7.0803	21.5654
124.694	1.471154	- 6.4785	20.9145
149.550	1.563067	- 5.9102	20.2371

Table IV

	S, S <sub>1</sub>		C <sub>2</sub> H <sub>6</sub>	
	S in joules mole <sup>-1</sup> degree C <sup>-1</sup>			
T/d	0°C	S <sub>1</sub>	25°C	S <sub>1</sub>
0	∞	0	∞	0
1	0	-.001	3.635	-.076
2	-5.844	-.162	-2.204	-.151
3	-9.297	-.244	-5.651	-.227
5	-13.708	-.408	-10.049	-.378
10	-19.886	-.802	-15.190	-.756
15	-23.679	-.244	-19.939	-.133
20	-26.500	-.167	-22.708	-.150
40			-29.974	-.013
60			-34.838	-.506
80				-.54280
100				-37.277
120				-55.860
140				-42.146
160				-44.223
180				-46.165
				-10.280
				-41.935
				-9.603
	100°C		125°C	
	∞	0	∞	0
0	∞	0	∞	0
1	14.324	-.055	17.851	-.052
2	8.506	-.110	12.036	-.104
3	5.080	-.166	8.613	-.156
5	.723	-.275	4.262	-.260
10	-5.314	-.549	-1.760	-.519
15	-8.958	-.821	-5.388	-.776
20	-11.620	-.1092	-8.036	-.031
40	-18.450	-2.158	-14.807	-2.040
60	-22.860	-3.198	-19.163	-3.024
80	-26.264	-4.210	-22.516	-3.986
100	-29.108	-5.198	-25.323	-4.937
120	-31.595	-6.169	-27.786	-5.885
140	-33.842	-7.135	-30.024	-6.841
160	-35.930	-8.112	-32.113	-7.819
180	-37.919	-9.123	-34.109	-8.836
	150°C			
	∞	0	∞	0
0	∞	0	∞	0
1	21.368	-.051	21.368	-.051
2	15.554	-.102	15.554	-.102
3	12.132	-.153	12.132	-.153
5	7.783	-.255	7.783	-.255
10	1.767	-.508	1.767	-.508
15	-1.855	-.759	-1.855	-.759
20	-4.497	-1.009	-4.497	-1.009
40	-11.240	-1.989	-11.240	-1.989
60	-15.564	-2.942	-15.564	-2.942
80	-18.891	-3.877	-18.891	-3.877
100	-21.676	-4.807	-21.676	-4.807
120	-24.127	-5.741	-24.127	-5.741
140	-26.359	-6.692	-26.359	-6.692
160	-28.449	-7.671	-28.449	-7.671
180	-30.442	-8.686	-30.442	-8.686

Table V

U, $U_1$				$C_2H_5$				
<u>U in joule mole<sup>-1</sup></u>								
T / d	0°C		25°C		50°C		75°C	
	U	$U_1$	U	$U_1$	U	$U_1$	U	$U_1$
0	44.8	0	1081.3	0	2193.7	0	3386.0	0
1	0	-44.8	1038.1	-43.3	2152.8	-40.8	3347.6	-38.4
2	-44.8	-89.5	994.9	-86.5	2112.1	-81.6	3309.2	-76.8
3	-89.6	-134.3	951.7	-129.6	2071.4	-122.3	3271.0	-115.0
5	-179.3	-224.1	865.6	-215.7	1990.3	-203.	3194.6	-191.4
10	-404.1	-448.8	651.3	-430.0	1788.8	-404.8	3005.2	-380.3
15	-629.6	-674.3	438.5	-642.8	1589.4	-604.3	2817.7	-568.5
20	-855.8	-900.5	227.2	-854.1	1301.9	-801.8	2632.2	-753.8
40			-603.6	-1684.9	62.1	-1572.6	1909.0	-1477.0
60			-1409.2	-2490.5	-116.6	-2310.3	1217.6	-2168.4
80					-814.8	-3008.4	560.4	-2825.6
100					-1468.0	-3661.7	-62.3	-3448.3
120					-2076.5	-4270.2	-651.5	-4037.5
140					-2645.6	-4839.2	-1213.2	-4599.2
160					-3183.9	-5377.6	-1754.0	-5140.0
180					-3702.5	-5896.2	-2282.5	-5668.5

	<u>100°C</u>		<u>125°C</u>		<u>150°C</u>	
0	4661.1	0	6020.4	0	7464.0	0
1	4624.6	- 36.5	5985.1	- 35.3	7429.2	- 34.9
2	4588.3	- 72.9	5949.9	- 70.5	7394.4	- 69.7
3	4551.9	- 109.2	5914.7	- 105.6	7359.6	- 104.4
5	4479.5	- 181.6	5844.6	- 175.7	7290.4	- 173.6
10	4299.8	- 361.4	5670.7	- 349.7	7118.7	- 345.3
15	4121.8	- 539.3	5498.5	- 521.9	6948.9	- 515.1
20	3945.7	- 715.4	5328.1	- 692.3	6730.9	- 683.1
40	3259.1	-1402.0	4663.8	-1356.6	6128.2	-1335.8
60	2601.9	-2059.2	4028.0	-1992.4	5504.7	-1959.3
80	1974.0	-2687.1	3419.3	-2601.1	4978.1	-2555.9
100	1574.7	-3286.4	2832.3	-3188.0	4550.8	-3153.5
120	801.7	-3859.4	2265.6	-3754.7	3769.5	-3694.5
140	244.9	-4416.2	1713.8	-4306.6	3220.7	-4244.3
160	- 296.9	-4958.1	1171.4	-4849.0	2677.3	-4786.7
180	- 832.2	-5493.3	633.7	-5386.7	2140.5	-5323.5

Table VIH in joule mole<sup>-1</sup>

H

C<sub>2</sub>H<sub>5</sub>

T/d	0°C	25°C	50°C	75°C	100°C	125°C	150°C
0	67.4	1311.8	2632.0	4032.2	5515.2	7082.3	8733.8
1	0	1247.9	2572.3	3976.5	5462.9	7032.5	8685.7
2	- 67.3	1184.1	2512.7	3921.0	5410.7	6981.8	8637.8
3	- 134.5	1120.5	2453.3	3865.6	5358.8	6933.4	8589.6
5	- 268.8	993.8	2335.2	3755.4	5255.4	6835.0	8495.0
10	- 603.2	679.9	2043.0	3483.1	4999.8	6591.8	8260.4
15	- 935.9	370.2	1755.3	3215.3	4748.5	6352.7	8029.9
20	-1266.9	64.6	1472.3	2951.8	4501.3	6117.7	7803.5
40		-1116.0	385.8	1942.5	3555.3	5219.0	6940.2
60		-2227.9	- 625.8	1004.5	2676.7	4385.4	6141.6
80			-1555.4	139.8	1864.4	3615.1	5405.9
100			-2399.9	- 653.1	1116.6	2902.3	4725.8
120			-3162.1	-1377.5	430.3	2245.6	4099.1
140			-3852.1	-2040.7	- 204.7	1641.2	3524.7
160			-4479.4	-2648.5	- 786.5	1088.0	3001.0
180			-5058.9	-3208.9	-1320.5	586.7	2535.4

Table VIIF in joule mole<sup>-1</sup>

F

C<sub>2</sub>H<sub>6</sub>

T/d	0°C	25°C	50°C	75°C	100°C	125°C	150°C
0	∞	∞	∞	∞	∞	∞	∞
1	0	- 45.6	- 181.4	- 406.5	- 720.4	-1122.3	-1612.9
2	1551.6	1652.0	1662.0	1582.6	1414.3	1157.7	812.5
3	2449.9	2636.5	2732.7	2739.1	2656.5	2485.5	2225.9
5	3565.1	3861.8	4067.6	4183.5	4209.9	4147.8	3996.9
10	5027.8	5478.4	5837.2	6105.1	6282.8	6371.4	6371.0
15	5838.3	6383.2	6835.1	7195.3	7464.4	7643.8	7754.0
20	6382.6	7008.7	7518.0	7945.8	8281.7	8527.5	8683.8
40		8533.1	9033.0	9635.8	10143.6	10559.3	10884.4
60		8977.6	9796.1	10513.1	11132.2	11657.5	12090.8
80			10263.0	11069.3	11774.5	12384.2	12902.1
100			10578.2	11458.2	12236.4	12914.6	13503.1
120			10804.1	11748.0	12591.5	13328.8	13978.7
140			10973.9	11974.6	12873.1	13667.9	14374.7
160			11106.9	12159.6	13110.2	13957.2	14715.3
180			11215.6	12317.2	13317.4	14214.2	15022.2

Table VIII

T/d	G							C <sub>2</sub> H <sub>6</sub>
	0°C	25°C	50°C	75°C	100°C	125°C	150°C	
0	∞	∞	∞	∞	∞	∞	∞	∞
1	0	164.6	238.0	222.4	117.8	- 74.9	- 356.4	
2	1529.0	1841.2	2062.7	2194.4	2236.7	2190.7	2056.0	
3	2405.0	2805.3	3114.6	3333.8	3463.3	3504.2	3456.3	
5	3475.6	3990.0	4412.5	4744.3	4985.8	5138.2	5201.5	
10	4828.6	5507.0	6091.3	6583.0	6982.8	7292.5	7512.6	
15	5532.0	6314.9	7001.1	7592.8	8091.0	8498.1	8815.0	
20	5971.5	6834.9	7598.4	8255.4	8857.3	9317.2	9706.3	
40		7820.7	8797.7	9669.3	10439.9	11114.5	11696.3	
60		8159.0	9287.0	10300.0	11207.0	12014.9	12727.7	
80			9522.3	10643.7	11665.0	12580.0	13399.8	
100				9646.3	10867.4	11978.3	12984.6	13981.1
120					11022.0	12219.9	13308.8	14303.4
140					9718.5			
160					9767.3	11147.0	12423.6	13595.2
180					9811.4	11265.0	12620.7	13873.8
					9859.3	11390.8	12829.4	14167.2
								15417.1

Table IX

T/d	ΔK						
	0°C	25°C	50°C	75°C	100°C	125°C	150°C
0	0	0	0	0	0	0	0
1	- 23.1	- 18.8	- 15.9	- 13.4	- 11.0	- 8.2	- 4.8
2	- 45.9	- 37.3	- 31.5	- 26.6	- 21.9	- 16.2	- 9.4
3	- 68.3	- 55.5	- 46.9	- 39.6	- 32.5	- 24.0	- 13.8
5	- 112.2	- 91.2	- 76.9	- 64.8	- 53.1	- 39.0	- 22.0
10	- 216.4	- 175.7	- 147.8	- 124.1	- 100.7	- 72.7	- 39.0
15	- 312.6	- 253.6	- 212.9	- 177.7	- 142.8	- 101.2	- 51.1
20	- 400.6	- 324.9	- 271.9	- 225.9	- 179.8	- 124.5	- 58.5
40		- 543.7	- 448.3	- 361.1	- 271.2	- 163.5	- 37.8
60		- 656.9	- 532.1	- 409.3	- 278.6	- 121.2	+ 61.1
80			- 528.5	- 374.8	- 203.7	+ 2.8	+ 240.3
100			- 448.8	- 262.8	- 50.0	+ 212.3	+ 509.1
120			- 301.6	- 79.0	+ 183.1	+ 509.1	+ 874.2
140			- 95.4	+ 178.1	+ 505.5	+ 302.9	+ 1347.1
160			+ 176.1	+ 517.9	+ 927.3	+ 1413.0	+ 1948.6
180			+ 512.2	+ 951.0	+ 1467.0	+ 2059.9	+ 2698.7

Table X $C_v$  in joule mole<sup>-1</sup> degree C<sup>-1</sup>

<u>T/d</u>	<u>0°C</u>	<u>25°C</u>	<u>50°C</u>	<u>75°C</u>	<u>100°C</u>	<u>125°C</u>	<u>150°C</u>
0	40.0	42.94	46.07	49.34	52.68	56.06	59.43
1	40.1	43.03	46.17	49.43	52.74	56.09	59.44
2	40.1	43.12	46.27	49.52	52.81	56.12	59.44
3	40.1	43.21	46.37	49.61	52.87	56.15	59.45
5	40.3	43.42	46.56	49.79	53.00	56.21	59.47
10	40.7	43.90	47.07	50.22	53.31	56.37	59.50
15	41.3	44.5	47.58	50.70	53.62	56.53	59.55
20	42.1	45.0	48.07	51.14	53.93	56.68	59.63
40		47.6	50.22	52.83	55.12	57.35	59.96
60		51.6	52.45	54.46	56.24	58.01	60.37
80			53.80	55.72	57.21	58.57	60.7
100			55.32	56.95	57.86	58.98	60.5
120			56.29	57.66	58.35	59.21	61.4
140			56.8	57.8	58.5	59.4	61.3
160			56.5	57.8	58.5	59.3	61.3
180			56.1	57.5	58.3	59.2	61.4

Table XI $C_p$  in joules mole<sup>-1</sup> degree C<sup>-1</sup>

<u>T/d</u>	<u>0°C</u>	<u>25°C</u>	<u>50°C</u>	<u>75°C</u>	<u>100°C</u>	<u>125°C</u>	<u>150°C</u>
0	48.3	51.44	54.38	57.65	61.00	64.37	67.74
1	48.7	51.64	54.74	57.96	61.26	64.58	67.92
2	49.1	52.04	55.09	58.28	61.52	64.80	68.09
3	49.5	52.45	55.45	58.61	61.79	64.95	68.27
5	50.4	53.32	56.23	59.28	62.34	65.45	69.64
10	53.1	55.69	58.30	61.05	63.73	66.60	69.58
15	56.7	58.5	60.60	62.95	65.32	67.83	70.59
20	61.5	61.8	63.14	65.03	66.96	69.14	71.66
40		83.1	77.18	75.27	74.74	75.17	76.56
60		135.9	100.32	89.34	84.46	82.28	82.12
80			136.13	107.15	95.56	89.91	87.8
100			190.51	127.23	106.50	97.11	93.0
120			253.58	144.85	115.34	106.64	97.2
140			297.1	153.8	120.1	105.7	99.3
160			285.4	153.2	119.9	105.9	99.6
180			261.2	145.6	116.7	104.4	98.7